

Second Midterm Examination, CH20B, Winter 2018

1 March, 7:00 – 8:50 pm

10 am

11 am

in problems. Your grade will be based on your scores for Problem 1 or for Problem 2, whichever of these is higher. You will have fifty minutes to complete the exam. You may use a scientific calculator, and a noncommunicating calculator of your choice is acceptable. Since this exam is eligible for any possible regrade, you must work in pencil.

Problem 1: 20 of 20 points

OR

Problem 2: 18 of 20 points

Problem 3: 20 of 20 points

Problem 4: 15 of 15 points

Problem 5: 15 of 15 points

Problem 6: 15 of 15 points

Problem 7: 15 of 15 points

$$R = 8.314 \text{ J/mol-K} = 0.08314 \text{ L-bar/mol-K} = 0.08206 \text{ L-atm/mol-K}$$

$$\text{Avogadro's number} = 6.022 \times 10^{23} \text{ mol}^{-1}$$

S° values at 298.15 K:

$$\text{C}_6\text{H}_6(g): 269.2 \text{ J/mol-K}$$

$$\text{C}_6\text{H}_6(l): 172.8 \text{ J/mol-K}$$

ΔH_f° values at 298.15 K:

$$\text{C}_6\text{H}_6(g): 82.93 \text{ kJ/mol}$$

$$\text{C}_6\text{H}_6(l): 49.03 \text{ kJ/mol}$$

$$\text{CO}_2(g): -393.51 \text{ kJ/mol}$$

$C_{P,m}$ (i.e., molar constant-pressure heat capacity) values:

$$\text{C}_6\text{H}_6(g): 81.6 \text{ J/mol-K}$$

$$\text{C}_6\text{H}_6(l): 136 \text{ J/mol-K}$$

$$\text{CO}_2(g): 37.11 \text{ J/mol-K}$$

$$\text{O}_2(g): 29.36 \text{ J/mol-K}$$

$$\text{C}(s, \text{graphite}): 8.53 \text{ J/mol-K}$$

$$\text{H}_2\text{O}(l): 75.29 \text{ J/mol-K}$$

$$\text{H}_2\text{O}(s): 37.98 \text{ J/mol-K}$$

$$\text{Ar}(g): 20.79 \text{ J/mol-K}$$

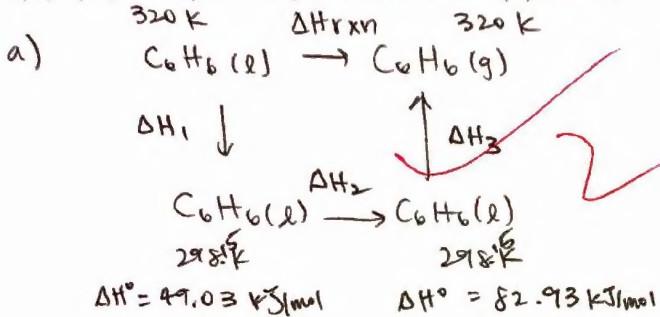
1. Consider the process



at 320 K and 1 atm.

- (a) (15 points) Determine (i) ΔH° , (ii) ΔS° and (iii) ΔG° for this process. You may take all relevant heat capacities to be independent of temperature. You **may not** assume that ΔH , ΔS , or ΔG values are independent of temperature.

- (b) (5 points) From your answer to (a) determine the vapor pressure of $C_6H_6(l)$ at 320 K.



$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \Delta H_3$$

$$\Delta H_1 = n c_p \Delta T = 1 \left(\frac{136 \text{ J}}{\text{mol} \cdot \text{K}} \right) (298.15 - 320)$$

$$= -2971.6 \text{ J/mol}$$

$$\Delta H_2 = 1 \Delta H_g^\circ - 1 \Delta H_l^\circ = 33.9 \text{ kJ/mol}$$

$$= 33900 \text{ J/mol}$$

i) $\Delta H^\circ = 1782.962 \text{ J}$

$$\Delta H^\circ = -2971.6 \text{ J/mol} + 33900 \text{ J/mol}$$

$$\Delta H^\circ = 32711.36 \text{ J/mol}$$

$$\Delta H_3 = n c_p \Delta T = 1 \left(\frac{81.6 \text{ J}}{\text{mol} \cdot \text{K}} \right) (320 - 298.15)$$

$$= 1782.96 \text{ J/mol}$$

ii) $\Delta S_1 = n c_p \ln \left(\frac{T_2}{T_1} \right) = \frac{136 \text{ J}}{\text{mol} \cdot \text{K}} \ln \left(\frac{298.15}{320} \right) = -9.6185 \text{ J/mol}$

$$\Delta S_3 = n c_p \ln \left(\frac{T_2}{T_1} \right) = \frac{81.6 \text{ J}}{\text{mol} \cdot \text{K}} \ln \left(\frac{320}{298.15} \right) = 5.7711$$

$$\Delta S = 9.6185 + 5.7711 + 96.4$$

$$\Delta S_2 = 269.2 \text{ J/mol} - 172.8 \text{ J/mol} = 96.4$$

$$\Delta S^\circ = 92.55 \text{ J/mol}$$

iii) $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = (32711.36 \text{ J/mol}) - 320 \text{ K} (92.55 \text{ J/mol})$

$$\Delta G^\circ = 3095.36 \text{ J}$$

b) at normal boiling pt, vapor pressure = 1 atm, $\Delta h = 0$

$$0 = 32711.36 - T (92.55)$$

$$T = 353.435 \text{ K}$$

$$\ln \left(\frac{P_2}{P_1} \right) = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln \left(\frac{P_2}{1} \right) = -\frac{32711.36}{8.314} \left[\frac{1}{320} - \frac{1}{353.435} \right]$$

$$\ln P_2 = -1.1631466$$

$$P_2 = 0.3125 \text{ atm}$$

vapor pressure @ 320 K

is 0.3125 atm

0.31 atm w/ sig fig

2. (20 points) 1.00 mol of $\text{H}_2\text{O}(s)$ at 265 K, 1 atm is placed in 10.00 mol of $\text{H}_2\text{O}(l)$ at 300 K, 1 atm in a thermally insulated container. The system is allowed to come to equilibrium at constant pressure. Determine the final temperature of the system and then compute the change in entropy (ΔS) of the H_2O for this process. Note that $\Delta H_{\text{fus}}^{\circ} = 6.009 \text{ kJ/mol}$ at 273 K, the normal melting point of water.

$$q_{\text{total}} = 0$$

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$q_{\text{H}_2\text{O}(s)} + q_{\text{heat}} + q_{\text{H}_2\text{O}(l)} = 0$$

$$0 = 1 \text{ mol} \left(\frac{37.98 \text{ J}}{\text{mol} \cdot \text{K}} \right) (273 \text{ K} - 265 \text{ K}) + 1 \text{ mol} \left(\frac{6009 \text{ J}}{\text{mol}} \right) + 10 \text{ mol} \left(\frac{75.29 \text{ J}}{\text{mol} \cdot \text{K}} \right) (T_f - 273 \text{ K}) \\ + 1 \text{ mol} \left(\frac{75.29 \text{ J}}{\text{mol} \cdot \text{K}} \right) (T_f - 273 \text{ K}) + 10 \text{ mol} \left(\frac{75.29 \text{ J}}{\text{mol} \cdot \text{K}} \right) (T_f - 300 \text{ K})$$

$$0 = 303.84 + 6009 + 75.29 T_f - 20554.17 + 752.9 T_f - 225870$$

$$0 = 828.19 T_f - 246120.33$$

$$828.19 T_f = 246120.33 \quad \text{H}_2\text{O}(l) C_p = 75.29$$

$$T_f = 297.18 \text{ K}, \quad \text{w/ sig fig} \quad T_f = 300 \text{ K}$$

$$T_f = \frac{297.18 \text{ K}}{828.19 \text{ J/K}}$$

$$\text{H}_2\text{O}(s) C_p = 37.98$$

$$\Delta S_{\text{total}} = \Delta S_{\text{ice, heat}} + \Delta S_{\text{ice, melt}} + \Delta S_{\text{water, warm}} + \Delta S_{\text{water, cool}} \\ = 1 \text{ mol} (37.98) \ln\left(\frac{273}{265}\right) + \frac{6009}{273} + 1 (75.29) \ln\left(\frac{297.18}{273}\right) \\ + 10 (75.29) \ln\left(\frac{297.18}{300}\right) \rightarrow 1.944 \text{ J/K w/ sig fig}$$

$$= 1.944 \text{ J/K} \rightarrow 2 \text{ J/K w/ sig fig}$$

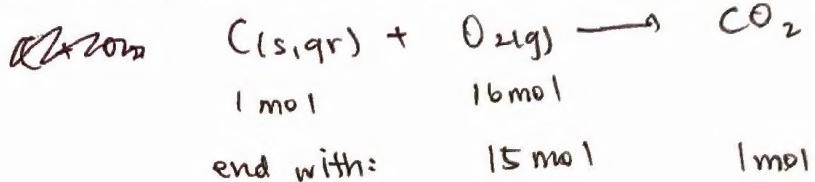
$$\Delta S_{\text{total}} = 22.419 \text{ J/K}$$

$$\rightarrow 20 \text{ J/K w/ sig fig}$$

3. (20 points) 1.00 mol C(s, graphite) and 16 mol O₂(g) are initially present in a thermally insulated container at 298.15 K and 1 atm. The C(s) is ignited and complete combustion of the C(s) to CO₂(g) occurs, leaving the contents of the container at 1 atm. (That is, the process occurs at constant pressure.) Determine the final temperature of the container contents. You may assume that all relevant heat capacities are independent of temperature and that the container has zero heat capacity.

$$q_f = 0$$

$$\Delta H = q_p$$



$$\Delta H_{rxn} + q_{O_2} + q_{CO_2} = 0$$

$$\Delta H_{rxn} = (-393.51 \text{ kJ/mol}) \cdot (1 \text{ mol}) - 0 = -393.51 \text{ kJ} = -393510 \text{ J}$$

$$q_{O_2} = n_{O_2} \left(\frac{29.36 \text{ J}}{\text{mol} \cdot \text{K}} \right) (T_f - 298.15 \text{ K})$$

$$q_{CO_2} = n_{CO_2} \left(\frac{37.11 \text{ J}}{\text{mol} \cdot \text{K}} \right) (T_f - 298.15 \text{ K})$$

$$0 = -393510 + 15 \left(\frac{29.36 \text{ J}}{\text{K}} \right) (T_f - 298.15 \text{ K}) + 1 \left(\frac{37.11 \text{ J}}{\text{K}} \right) (T_f - 298.15 \text{ K})$$

$$= -393510 + 440.4 T_f - 131305.26 + 37.11 T_f - 11064.3465$$

$$535879.6065 = 477.51 T_f$$

$$T_f = 1122.2 \text{ K}$$

1100 K w/ 2 sig fig

4. The equilibrium constant for the reaction



at 298 K is 5.9×10^{-13} .

(a) (5 points) Determine ΔG° for the reaction at 298 K.

(b) (10 points) Suppose a rigid container held at 298 K initially contains only $\text{NO}_2(g)$ at 1.0 atm. Determine the partial pressures of $\text{NO}_2(g)$, $\text{NO}(g)$, and $\text{O}_2(g)$ once equilibrium is established. (Hint: Look for reasonable approximations to simplify the algebra.)

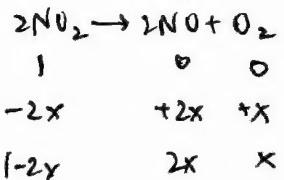
$$\text{a) } \Delta G^\circ = -RT \ln K$$

$$= -\frac{8.314 \text{ J}}{\text{K mol}} (298 \text{ K}) \ln (5.9 \times 10^{-13})$$

$$= 69765.09236 \text{ J/mol rxn}$$

$$\Delta G^\circ = 7.0 \times 10^4 \text{ J/mol rxn}$$

$$\text{b) } \cancel{\text{At } 0^\circ} \quad K = \frac{(P_{\text{O}_2})(P_{\text{NO}})^2}{(P_{\text{NO}_2})^2}$$



$$5.9 \times 10^{-13} = \frac{(x)(2x)^2}{(1-2x)^2}$$

because K is
so ~~large~~^{small},
 x must be very
large, small,
so $1-2x \approx 1$

$$5.9 \times 10^{-13} = \frac{4x^3}{1}$$

$$1.475 \times 10^{-13} = x^3$$

$$x = 5.2836 \times 10^{-5} \text{ atm}$$

$$P_{\text{O}_2} = 5.3 \times 10^{-5} \text{ atm}$$

$$(\rightarrow 5.2836 \times 10^{-5} \text{ atm})$$

$$P_{\text{NO}} = 1.06 \times 10^{-4} \text{ atm}$$

$$(\rightarrow 1.0567 \times 10^{-4} \text{ atm})$$

$$P_{\text{NO}_2} = 1 \text{ atm}$$

$$(\rightarrow 0.9999 \text{ atm})$$

{ with sig fig }

{ without sig fig }

5. 1.00 mol of Ar(g) confined by a moveable, frictionless piston in a cylinder at 400 K and 1 atm is cooled reversibly to 300 K.

(a) (8 points) Determine q , w , ΔU , and ΔH for this process treating the Ar(g) as the system. (You may assume that all relevant heat capacities are independent of temperature.)

(b) (7 points) Determine the entropy change (ΔS) of the Ar(g) and that of the surroundings (ΔS_{surr}) for this process. (Hint: Remember what the 2nd Law says about ΔS_{tot} for a reversible process.)

$$a) \Delta H = nC_p \Delta T = 1 \text{ mol} \left(\frac{20.79 \text{ J}}{\text{mol K}} \right) (300 \text{ K} - 400 \text{ K}) = -2079 \text{ J}$$

$$\Delta H = q_{\text{fp}} = -2079 \text{ J} \rightarrow 2079 \text{ J released} \quad V_1 = 1 \text{ L} (0.08206)(400) = 32.824 \text{ L}$$

$$\frac{T_1}{T_2} = \frac{V_1}{V_2} \rightarrow \frac{400}{300} = \frac{32.824}{V_2}$$

$$V_2 = 24.618 \text{ L}$$

$$PV_1 = nRT_1$$

$$= 1 \text{ mol} (0.08206)(400) = 32.824 \text{ L} \cdot \text{atm}$$

$$W = -P\Delta V$$

$$= -1 (32.824 \text{ L} \cdot \text{atm} + 24.618 \text{ L} \cdot \text{atm})$$

$$= -8.206 \text{ L} \cdot \text{atm} \cdot \frac{101.325 \text{ J}}{\text{L} \cdot \text{atm}}$$

$$= -831.47295 \text{ J}$$

831.47295 J done on gas

~~ΔU = q + w~~

$$\therefore \Delta U = q_f + w$$

$$= -2079 \cancel{J} + 831.47295 \text{ J}$$

$$\Delta H = -2079 \text{ J} + 2 = -1247.5 \text{ J} + 2$$

$$q = -2079 \text{ J, or } 2079 \text{ J heat released} + 2$$

$$w = -831.47295 \text{ J, or } 831.47295 \text{ J work done on gas}$$

$$\Delta U = -1247.5 \text{ J} + 2$$

alternatively:

$$\Delta U = nC_v \Delta T$$

$$C_v + R = C_p - R$$

$$\Delta U = 1 (20.79 - 8.315)(300 - 400) = -1247.5 \text{ J}$$

see back side for part b

b) *for reversible processes, $\Delta S_{\text{tot}} = 0 = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \rightarrow \Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$

~~ΔS_{sys} = ΔS_{surr}~~ ~~= TΔS_{sys}~~

$$\Delta S_{\text{sys}} = \Delta S_{\text{surr}} = nC_p \ln \left(\frac{T_2}{T_1} \right) = 1 \text{ mol} \left(\frac{20.79 \text{ J}}{\text{mol K}} \right) \ln \left(\frac{300}{400} \right)$$

$$\Delta S_{\text{sys}} = 5.981 \text{ J/K}$$

$$\Delta S_{\text{sys}} = nC_p \ln \frac{T_2}{T_1}$$

$$= 1 \text{ mol} \left(\frac{20.79 \text{ J}}{\text{mol K}} \right) \ln \left(\frac{300}{400} \right)$$

$$\Delta S_{\text{surr}} = \frac{5.981 \text{ J}}{1000 \text{ K}}$$

5.b) For rev. processes, $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

$$\Delta S_{\text{sys}} = \Delta S_{\text{Ar(g)}} = n C_p \ln \left(\frac{T_2}{T_1} \right)$$

$$= 1 \text{ mol} \left(\frac{20.79 \text{ J}}{\text{mol K}} \right) \ln \left(\frac{300}{400} \right)$$

$$\boxed{\Delta S_{\text{Ar(g)}} = -5.98 \text{ J/K}}$$

$$\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$$

$$-5.98 \text{ J/K} = -\Delta S_{\text{surr}} \quad +7$$

$$\boxed{\Delta S_{\text{surr}} = 5.98 \text{ J/K}}$$

6. (15 points) Complete combustion of 5.000 g of compound containing only C, H, and O yields 11.375 g of CO_2 and 4.646 g of H_2O . When 10.0 g of the compound is dissolved in 300.0 g of $\text{H}_2\text{O}(l)$ the solution has a freezing point that is 1.07 K lower than that of pure $\text{H}_2\text{O}(l)$. Determine the molecular formula of the compound. (Assume that the solution is ideal and that $K_f = 1.86 \text{ K}\cdot\text{kg/mol}$ for $\text{H}_2\text{O}(l)$). Note also that the molar mass of CO_2 is 44.01 g/mol, that of H_2O is 18.02 g/mol, that of C is 12.011 g/mol, that of H is 1.008 g/mol, and that of O is 16.0 g/mol.)

$$11.375 \text{ g } \text{CO}_2 \cdot \frac{\text{mol } \text{CO}_2}{44.01 \text{ g } \text{CO}_2} \cdot \frac{1 \text{ mol C}}{\text{mol } \text{CO}_2} = 0.25846 \text{ mol C} = 3.1044 \text{ g C}$$

$$4.646 \text{ g } \text{H}_2\text{O} \cdot \frac{\cancel{18.02} \text{ mol } \text{H}_2\text{O}}{\cancel{18.02} \text{ g } \text{H}_2\text{O}} \cdot \frac{2 \text{ mol H}}{\text{mol } \text{H}_2\text{O}} = 0.515649 \text{ mol H} = 0.51977 \text{ g H}$$

$$5 - 3.1044 - 0.51977 = 1.375814598 \text{ g O} \cdot \frac{\text{mol O}}{16 \text{ g O}} = 0.085988 \text{ mol O}$$

$$\frac{0.25846 \text{ mol C}}{0.085988 \text{ mol O}} = \frac{3 \text{ mol C}}{1 \text{ mol O}} \quad \text{C}_3\text{H}_6\text{O} \rightarrow 58.081 \text{ g/mol}$$

$$\frac{0.515649 \text{ mol H}}{0.085988 \text{ mol O}} > \frac{6 \text{ mol H}}{(\text{mol O})}$$

Freezing pt depression

let $x = \text{unknown molar mass}$

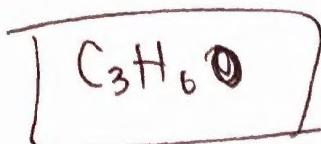
$$\Delta T_f = K_f m$$

$$1.07 \text{ K} = \left(\frac{1.86 \text{ K kg}}{\text{mol}} \right) \left(\frac{\frac{10 \text{ g}}{x}}{0.3 \text{ kg}} \right)$$

$$1.07 = \frac{62 \text{ g}}{\text{mol } x}$$

$$x = 57.9439 \frac{\text{g}}{\text{mol}}$$

57.9 is very close to 58.081



7. The vapor pressure of pure $C_6H_6(l)$ at 300 K is 0.1355 atm and that of pure $C_6H_{14}(l)$ is 0.2128 atm. A solution composed of 100.0 g of $C_6H_6(l)$ and 50.0 g of $C_6H_{14}(l)$ is prepared at 300 K. Treat that solution as ideal to answer the following. (Note that the molar mass of C_6H_6 is 78.11 g/mol and that of C_6H_{14} is 86.18 g/mol.)

(a) (7 points) Determine the total vapor pressure of the solution.

(b) (8 points) Determine the mole fraction of C_6H_{14} in the vapor above the solution.

$$a) 100 \text{ g } C_6H_6 \cdot \frac{\text{mol}}{78.11 \text{ g}} = 1.280245807 \text{ mol } C_6H_6 \quad \text{total moles} = 1.8604268 \text{ mol}$$

$$50 \text{ g } C_6H_{14} \cdot \frac{\text{mol}}{86.18 \text{ g}} = 0.5801810165 \text{ mol } C_6H_{14}$$

$$X_{C_6H_{14},\text{sol.}} = \frac{1.280245807}{1.8604268} = 0.688146$$

$$X_{C_6H_{14},\text{sol.}} = \frac{0.5801810165}{1.8604268} = 0.311853715$$

$$P_{C_6H_6} = X_{C_6H_6} P^{\circ}_{C_6H_6} = (0.688146)(0.1355) = 0.0932438 \text{ atm}$$

$$P_{C_6H_{14}} = X_{C_6H_{14}} P^{\circ}_{C_6H_{14}} = (0.31185)(0.2128) = 0.0663625 \text{ atm}$$

$$\text{Total pressure} = P_{C_6H_6} + P_{C_6H_{14}} = 0.1596 \text{ atm}$$

$$b) X_{C_6H_{14},\text{vapor}} = \frac{0.663625}{0.1596} = 0.4158$$

15

Alternatively:

$$P_{\text{tot}} = 0.1596 \text{ atm} = \frac{n_{\text{tot}} RT}{V}$$

$$0.1596 = \frac{n_{\text{tot}}(0.08206)(300)}{V}$$

$$\frac{0.1596 V}{(0.08206)(300)} = n_{\text{tot}}$$

$$P_{C_6H_{14}} = 0.0663625 \text{ atm} = \frac{n_{C_6H_{14}} RT}{V}$$

$$n_{C_6H_{14}} = \frac{0.0663625 V}{0.08206 (300)}$$

$$X_{C_6H_{14},\text{vapor}} = \frac{\frac{0.0663625 V}{0.08206 (300)}}{0.1596 V} = \frac{0.4158}{0.08206 (300)}$$